



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08K 3/22, 7/00, C08F 2/44		A1	(11) International Publication Number: WO 99/35185 (43) International Publication Date: 15 July 1999 (15.07.99)
(21) International Application Number: PCT/NL99/00006 (22) International Filing Date: 8 January 1999 (08.01.99) (30) Priority Data: 1008003 9 January 1998 (09.01.98) NL (71) Applicant (for all designated States except US): NEDERLANDSE ORGANISATIE VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK ON- DERZOEK TNO [NL/NL]; Schoemakerstraat 97, NL-2628 VK Delft (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): FISCHER, Hartmut, Rudolf [DE/NL]; Dalkruid 13, NL-5731 TP Mierlo (NL). GIELGENS, Leon, Hubertus [NL/NL]; Catharijnesingel 100 DL, NL-3511 GV Utrecht (NL). (74) Agent: OTTEVANGERS, S., U.; Vereenigde Octrooibureaux, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <i>In English translation (filed in Dutch).</i>	
(54) Title: NANOCOMPOSITE MATERIAL			
(57) Abstract <p>The invention relates to a method for preparing a nanocomposite material based on a polymeric matrix and a layered double hydroxide, comprising the steps of: a) providing a layered double hydroxide which contains an amount of anions of at least 20 %, based on the total number of anions of the layered double hydroxide, which anions are compatible and/or reactive with the polymeric matrix; b) mixing the layered double hydroxide with a monomeric material for forming the polymeric matrix, in an amount such that the polymeric matrix is present in the nanocomposite material in an amount of at least 50 % by weight, based on the nanocomposite material; c) polymerizing the monomeric material to form the polymeric matrix. The invention further relates to a nanocomposite material obtainable by such method and to a shaped article manufactured from such nanocomposite material.</p>			

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Title: Nanocomposite material

The invention relates to a nanocomposite material, a method for the preparation of a nanocomposite material and to a shaped article of a nanocomposite material.

Over the past decades, it has already been frequently proposed to improve the properties of polymeric materials by incorporating a certain amount of a clay in those materials. The presence of a clay in a polymeric material is beneficial particularly to properties such as the mechanical strength and the heat resistance of the polymeric material.

10 To thus obtain a nanocomposite material that has the desired properties, it is important that the clay be dispersed in the polymeric material sufficiently homogeneously. This is not easy because the clay and the polymeric material are of a highly different nature. Polymers
15 constitute a normally non-polar, organic material, whereas the clay is a much more polar, inorganic material. Due to this difference, the materials exhibit poor miscibility with respect to each other; they are intrinsically non-miscible. In the literature, it has been proposed first to modify the
20 clay in different ways before it is mixed with a polymeric material. It has also been proposed to modify the clay and then to mix it with a monomeric material, which is thereupon polymerized in the presence of the clay.

In U.S. Patents 4,889,885 and 4,810,734, it is
25 described how a cationic clay is first modified with a swelling agent, which increases the interlayer distance of the clay structure. Used as swelling agents are surfactants, with a head group formed by an ammonium, pyridinium, sulfonium or phosphonium group, and one or more non-polar
30 tails. The cationic head group of the surfactant is exchanged with cations between the crystalline layers of the clay and the tails should be compatible with the polymeric material. Then the modified clay is mixed with monomeric material, which can enter into a bonding interaction with the tails of
35 the swelling agent. When, finally, the monomeric material is

then polymerized, the polymers are formed between the layers of the clay and a nanocomposite material is obtained.

A disadvantage of these known nanocomposite materials is that the quality of the end product is very highly
5 dependent on the quality of the clay used. Cationic clay is virtually always a natural product, which is not homogeneous in composition. This inhomogeneity of the clay leads to inhomogeneities in the composition of the nanocomposite material, which means that the desired properties are not
10 always achieved in a sufficient quality. It is therefore desirable to make it possible to incorporate into polymeric material a kind of clay that has a better controllable quality and composition.

U.S. Patent 5,658,653 describes a polymer composite
15 comprising a polymeric matrix in which a filler is incorporated. The polymeric matrix can be a polyolefin, polystyrene, polyurethane, epoxy resin, polyimide, polyacetal, polyester, polyvinyl, polyether or polyacryl. The filler is a mixed metal hydroxide that satisfies a specific
20 formula.

In order to enhance the compatibility of the polymeric material and the filler, the surface of the filler has been modified in that particular groups have been provided thereon. These groups can be, for instance, organic acids,
25 salts of sulfonic acids or phosphonic acids. It is also possible that anions of the filler have been exchanged with groups that form hydrogen bridges with the polymeric matrix.

A disadvantage of the material described in the above U.S. patent specification is that the filler is not
30 homogeneously dispersed in the polymeric matrix. This inhomogeneity is presumably due to the fact that only the surface of the filler is modified.

The object of the present invention is to provide a method for preparing a nanocomposite material comprising a
35 polymeric matrix in which a clay is incorporated, which nanocomposite material is very homogeneous in composition. It

is further contemplated for the clay to be of a kind that has a properly controllable quality and composition.

According to the invention, these objects are achieved by mixing a layered double hydroxide with monomeric material and polymerizing this in the presence of the layered double hydroxide. Layered double hydroxides are anionic clays, which, surprisingly, have presently been found to be modifiable so as to allow of homogeneous dispersion in a polymeric material.

Accordingly, the invention relates to a method for preparing a nanocomposite material based on a polymeric matrix and a layered double hydroxide, comprising the steps of

- a) providing a layered double hydroxide which contains an amount of anions of at least 20%, based on the total number of anions of the layered double hydroxide, which anions are compatible and/or reactive with the polymeric matrix;
- b) mixing the layered double hydroxide with a monomeric material for forming the polymeric matrix, in an amount such that the polymeric matrix is present in the nanocomposite material in an amount of at least 50% by weight, based on the nanocomposite material;
- c) polymerizing the monomeric material for forming the polymeric matrix.

It will be clear that the invention further relates to a nanocomposite material obtainable by the above method.

It has been found that a nanocomposite material prepared according to the present method has highly favorable properties. Thus, the heat resistance, the mechanical strength and the impact resistance of a polymeric material in which a layered double hydroxide is incorporated in accordance with the invention are strongly improved compared with the same properties of the polymeric material in which no layered double hydroxide is incorporated. It has further been found that the electrical conductivity and the permeability to gases and liquids, such as oxygen, water

vapor and hydrocarbons, have been reduced to a considerable extent. Since layered double hydroxides can be prepared synthetically, it is possible, according to the invention, to prepare a nanocomposite material of a constant, controllable
5 quality. It has furthermore been found that the *in situ* polymerization to form the polymeric matrix results in a very homogeneous product.

For that matter, it is known from U.S. Patent 4,558,102 that a particular kind of layered double hydroxide, a hydrotalcite, can be incorporated into a halogen-containing
10 rubber composition as an acid-acceptor to improve the water resistance of the rubber composition. Optionally, the hydrotalcite aggregates used can be modified with at most 10% by weight of a surfactant. What is involved here, however, is
15 only a modification of the surface of the aggregates, whereby the clay is not sufficiently modified to allow of homogeneous dispersion in the rubber composition.

Further, it is known to improve the properties of a hydrotalcite by incorporating a small amount of a polymeric
20 material. Challier et al., in J. Mater. Chem., 1994, 4, 367-371, have proposed to incorporate in a hydrotalcite a monolayer or bilayer of a polymeric material between each two layers of hydrotalcite to render the hydrotalcite electrically conductive.

25 A nanocomposite material according to the invention consists for the most part of the material of the polymeric matrix, comprising at least 50% and preferably at least 70% by weight of such material. Both homopolymers and copolymers can serve as polymeric matrix. It is one of the advantages of
30 the invention that through the choice of the anions of the layered double hydroxide, any polymeric matrix can be modified with a layered double hydroxide. Thus, by providing the appropriate ingredients, for instance in the form of a kit, those skilled in the art are enabled to prepare, for any
35 desired application, a combination of a particular layered

double hydroxide and a particular polymeric material, and thereby a desired nanocomposite material.

Polymeric materials suitable to serve as polymeric matrix in a nanocomposite material according to the invention are both poly-adducts and polycondensates. Preferably, the polymeric matrix has a degree of polymerization of at least 20, more preferably of at least 50. In this connection, for a definition of the degree of polymerization, reference is made to P.J. Flory, "Principles of Polymer Chemistry", New York, 1953. Examples are polyolefins, such as polyethylene or polypropylene, vinyl polymers, such as polystyrene, polymethyl methacrylate, polyvinyl chloride, polyvinylidene chloride or polyvinylidene fluoride, polyesters, such as polyethylene terephthalate or polycaprolactone, polycarbonates, polyaryl ethers, polysulfones, polysulfides, polyamides, polyether imides, polyether esters, polyether ketones, polyether ester ketones, polysiloxanes, polyurethanes and polyepoxides. Preferably used are polyolefins, vinyl polymers, polyesters, polycarbonates, polyamides, polyurethanes or polyepoxides, because the properties of these materials show a very strong improvement owing to the presence of a layered double hydroxide.

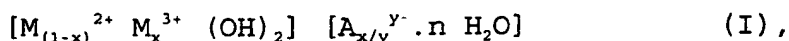
In a preferred embodiment, a polymeric matrix is formed from anionic monomeric material. According to this embodiment, anions of the layered double hydroxide are exchanged with anionic monomeric material, from which subsequently the polymeric matrix is formed in the presence of the layered double hydroxide. It has been found that according to this embodiment, a particularly homogeneous distribution of the layered double hydroxide in the polymeric matrix is obtained. Further, it is advantageous that no additional anions for compatibilizing the polymeric matrix and the layered double hydroxide are needed.

As stated, a nanocomposite material according to the invention is based, in addition to a polymeric matrix, on a layered double hydroxide (LDH). This material is a so-called

anionic clay, consisting of small crystalline sheets of dimensions of a few nanometers, between which anions are located. By these anions are meant anions other than hydroxyl groups. A layered double hydroxide can be both natural and synthetic in nature. For a description of possible methods of preparation for a synthetic layered double hydroxide, reference is made to U.S. Patents 3,539,306 and 3,650,704.

Preferably, the layered double hydroxide has a large contact surface and an ion exchange capacity of 0.5 to 6 milliequivalents per gram. An LDH preferably used is a hydrotalcite or a hydrotalcite-like material, because these materials can be readily prepared synthetically, while the desired properties can be eminently controlled.

Found to be uncommonly suitable are hydrotalcites that satisfy the formula (I):



wherein M^{2+} is a bivalent cation, M^{3+} is a trivalent cation, x is a number between 0.15 and 0.5, y is 1 or 2, n is a number from 1 to 10, and A is an anion selected from the group consisting of Cl^- , Br^- , NO_3^- , SO_4^{2-} and CO_3^{2-} . The bivalent cation is preferably selected from the group of bivalent magnesium, zinc, nickel, iron, copper, cobalt, calcium and manganese ions and combinations of these bivalent cations. Most preferably, the bivalent cation is a magnesium, zinc or calcium ion or a combination thereof. The trivalent cation is preferably selected from the group of trivalent aluminum, chromium, iron, cobalt and manganese ions and combinations of these trivalent cations. Most preferably, the trivalent cation is an aluminum, chromium or iron ion or a combination thereof.

Before a layered double hydroxide can be incorporated in a polymeric matrix for forming a nanocomposite material according to the invention, it should be modified so as to be compatible and/or reactive with the material of the polymeric matrix. To that end, the layered double hydroxide comprises at least 20%, preferably at least 60%, more preferably at

least 80%, based on the total number of anions of the layered double hydroxide, of an amount of anions that are reactive and/or compatible with the polymeric matrix. As has already been indicated, these anions can also be anionic monomers from which the polymeric matrix can be formed. The total number of anions on which the specified amounts of reactive and/or compatible anions are based is understood not to include the hydroxyl groups present in the layered double hydroxide.

It is particularly preferred that the layered double hydroxide contains at least 95%, based on the total number of anions of the layered double hydroxide, of an amount of anions that are reactive and/or compatible with the polymeric matrix. It has been found that a very homogeneous dispersion of the layered double hydroxide in the polymeric matrix is

obtained when such a large amount of reactive and/or compatible anions is present. This dispersion forms a nanocomposite material having uncommonly favorable properties.

In the preparation of a nanocomposite material according to the invention, it is preferred to grind or pulverize the layered double hydroxide beforehand. Such a pretreatment of the layered double hydroxide enables readier and better mixing of the various ingredients.

When a natural layered double hydroxide is used in a nanocomposite material according to the invention, this natural material will normally not contain the desired compatible and/or reactive anions. Therefore, the anions naturally present in natural hydrotalcites, such as chloride or nitrate ions, can be exchanged for the desired anions. If a synthetic layered double hydroxide is used, the desired anions may already have been introduced in the synthesis of the material. In the case of a synthetic layered double hydroxide, too, of course, the anions that are compatible and/or reactive with the polymeric matrix can be introduced by exchange. The exchange can be carried out in any known

manner, for instance as described by Sugahara et al., in Ceramics International, 14(1988), 163-167.

Preferably, the ion exchange is carried out by suspending the layered double hydroxide in water, whereafter
5 the pH of the suspension is reduced to a value of less than 4. Next, the anions with which the intended exchange is to be effected are added to the suspension and the pH is adjusted to a value in excess of 8. It has been found that this
10 procedure leads to a superior exchange product. Further, the procedure can be carried out readily and in a short time.

It has been found that a layered double hydroxide can be modified with anions that are solely compatible, solely reactive, or both, with the polymeric matrix, to obtain a
15 homogeneous dispersion of the layered double hydroxide in the polymeric matrix. Suitable compatible anions can be selected from anions of the formula RCOO^- , ROSO_3^- or RSO_3^- , wherein R
20 is an alkyl or an alkyl phenyl group having 6 to 22 carbon atoms, or combinations thereof, as well as from anionic monomers from which the polymeric matrix can be formed. One skilled in the art will be able to select suitable anions for
a polymeric material whose properties he seeks to improve by incorporating a layered double hydroxide.

Anions that are reactive with the polymeric matrix likewise satisfy the formula RCOO^- , ROSO_3^- or RSO_3^- , with the
25 proviso that the alkyl or alkyl phenyl chain comprises a reactive group. This reactive group can be present both attached to a terminal methylene group of the chain and at a different position in the chain. Therefore, the reactive
anions satisfy the formula $\text{R}'\text{-RCOO}^-$, $\text{R}'\text{-ROSO}_3^-$ or $\text{R}'\text{-RSO}_3^-$,
30 wherein R is a straight or branched alkyl or an alkyl phenyl group having 6 to 22 carbon atoms and R' is a reactive group selected from the group consisting of hydroxy, amino, epoxy, vinyl, isocyanate, carboxy, hydroxyphenyl and anhydride. The
choice of the reactive group can be suitably based by the
35 artisan on the nature of the material of the polymeric matrix. It has been found that a nanocomposite material based

on a layered double hydroxide that contains the reactive anions mentioned is exceptionally stable. Depending on the nature of the polymeric matrix, the reactive anions may also be compatible with the polymeric matrix, which yields a still
5 stabler nanocomposite material.

Bringing the ingredients together to form a nanocomposite material according to the invention can be carried out by any suitable method, provided such method yields a good mixing. As stated, the desired anions can be
10 provided in the layered double hydroxide during the synthesis thereof, or subsequently by ion exchange. If these anions are also monomers for forming the polymeric matrix, the layered double hydroxide can optionally be mixed with additional monomeric material in order to obtain the desired ratio of
15 polymeric matrix to layered double hydroxide. Examples of procedures for mixing monomeric material and layered double hydroxide comprise prolonged stirring at elevated temperature and extrusion. Suitable conditions for the mixing depend on the nature of the selected ingredients and can be simply
20 determined by the artisan. Stirring can be carried out, for instance, at a temperature between 40 and 80°C, and the extrusion, for instance, between 40 and 150°C in an extruder with a double screw.

The polymerization reaction in which the monomeric
25 material, in the presence of the layered double hydroxide, is converted to the polymeric matrix can be carried out in any known manner. It has been found that the presence of the layered double hydroxide hardly, if at all, has any disturbing influence on the polymerization reaction.

30 The nanocomposite materials according to the invention are particularly suitable to be used for a large variety of applications. The materials are eminently processable and can be shaped in conventional shaping steps, such as injection molding and extrusion processes. Shaped articles of a variety
35 of natures can be manufactured from the present nanocomposite material. Examples comprise any application for which the

material of the polymeric matrix is suited. As preferred applications, fibers, packaging materials and construction materials can be mentioned.

The invention will presently be further explained in
5 and by the following example.

Example I

Five grams of a hydrotalcite of the general formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ with an ion exchange capacity of about
10 4 mequ./g were suspended, together with 5 g α, ω -amino-undecanoic acid, in 200 ml water. The suspension obtained was stirred at 80°C for 3 hours. The precipitate that was formed was washed a few times with warm water and freeze-dried in the form of a white powder.

15 The white powder was mixed with 90 g caprolactam and 10 ml water and slowly heated to 260°C with stirring and under a dry nitrogenous atmosphere. After a 6-hour polycondensation, a transparent melt of a polyamide-6 was obtained. The transparency of the melt indicated that the
20 hydrotalcite was distributed completely and homogeneously in the polymeric matrix. The material was characterized with the aid of X-ray diffraction. The results showed that exfoliation of the hydrotalcite had occurred, since no reflection as a result of a periodicity of a layered sheet structure was
25 observed.

Claims

1. A method for preparing a nanocomposite material based on a polymeric matrix and a layered double hydroxide, comprising the steps of:
- 5 a) providing a layered double hydroxide which contains an amount of anions of at least 20%, based on the total number of anions of the layered double hydroxide, which anions are compatible and/or reactive with the polymeric matrix;
- 10 b) mixing the layered double hydroxide with a monomeric material for forming the polymeric matrix, in an amount such that the polymeric matrix is present in the nanocomposite material in an amount of at least 50% by weight, based on the nanocomposite material;
- c) polymerizing the monomeric material for forming the polymeric matrix.
- 15 2. A method according to claim 1, wherein the layered double hydroxide is a hydrotalcite or a hydrotalcite-like material.
3. A method according to claim 2, wherein the layered double hydroxide has an ion exchange capacity of 0.5 to
- 20 6 milliequivalents per gram and satisfies the formula (I)
- $$[M_{(1-x)}^{2+} M_x^{3+} (OH)_2] [A_{x/y}^{y-} \cdot n H_2O] \quad (I),$$
- wherein M^{2+} is a bivalent cation, M^{3+} is a trivalent cation, x is a number between 0.15 and 0.5, y is 1 or 2, n is a number from 1 to 10, and A is an anion selected from the group
- 25 consisting of Cl^- , Br^- , NO_3^- , SO_4^{2-} , and CO_3^{2-} .
4. A method according to claim 3, wherein M^{2+} is selected from the group consisting of Mg^{2+} , Zn^{2+} , Ni^{2+} , Fe^{2+} , Cu^{2+} , Co^{2+} , Ca^{2+} , Mn^{2+} and combinations thereof.
5. A method according to claim 3 or 4, wherein M^{3+} is
- 30 selected from the group consisting of Al^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+} , Mn^{3+} and combinations thereof.
6. A method according to claims 1-5, wherein the anions which are introduced into the layered double hydroxide in

step a) are also the monomeric material for forming the polymeric matrix.

7. A method according to claim 6, wherein the monomeric material is selected from the group of anionic monomers consisting of (meth)acrylates, carboxylic acids and amides.

8. A method according to claims 3-5, wherein the anions which are compatible and/or reactive with the polymeric matrix are selected from the group consisting of anions of the formula $R'-RCOO^-$, $R'-ROSO_3^-$ or $R'-RSO_3^-$, wherein R is a straight or branched alkyl or an alkyl phenyl group having 6 to 22 carbon atoms and R' is a hydrogen atom or a reactive group selected from the group consisting of hydroxy, amino, epoxy, vinyl, isocyanate, carboxy, hydroxyphenyl and anhydride.

9. A method according to claim 8, wherein in step a) an amount of at least 80%, preferably at least 95%, based on the total amount of anions of the layered double hydroxide, is exchanged.

10. A method according to any one of the preceding claims, wherein the polymeric matrix is present in an amount of at least 70% by weight, based on the nanocomposite material.

11. A method according to any one of the preceding claims, wherein the polymeric matrix has a degree of polymerization of at least 20.

12. A method according to claims 8-11, wherein the polymeric matrix is selected from the group consisting of polyolefins, vinyl polymers, polyesters, polycarbonates, polyamides, polyurethanes and polyepoxides.

13. A nanocomposite material obtainable by a method according to any one of the preceding claims.

14. A shaped article of a nanocomposite material according to claim 13.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/NL 99/00006

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K3/22 C08K7/00 C08F2/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 810 734 A (KAWASUMI MASAYA ET AL) 7 March 1989 cited in the application see example 1 see claim 1	1-14
A	WO 96 08526 A (CORNELL RES FOUNDATION INC) 21 March 1996 see claim 1	1-14
A	WO 93 11190 A (ALLIED SIGNAL INC) 10 June 1993 see claim 1	1-14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

6 May 1999

Date of mailing of the international search report

18/05/1999

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Siemens, T

INTERNATIONAL SEARCH REPORT

information on patent family members

nal Application No

PCT/NL 99/00006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4810734 A	07-03-1989	JP 1009202 A	12-01-1989
		JP 2098927 C	22-10-1996
		JP 7078089 B	23-08-1995
		DE 3810006 A	06-10-1995
WO 9608526 A	21-03-1996	US 5554670 A	10-09-1996
		AU 3419195 A	29-03-1996
		BR 9508914 A	03-11-1998
		CA 2199616 A	21-03-1996
		EP 0782593 A	09-07-1997
		JP 10505871 T	09-06-1998
		NO 971109 A	07-05-1997
WO 9311190 A	10-06-1993	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.